MODELING OF CATALYTIC COUPLING OF METHANE

Lucy M. Hair, William J. Pitz, Michael W. Droege and Charles K. Westbrook
Lawrence Livermore National Laboratory
P.O. Box 808   Livermore, CA 94551

Catalytic oxidative coupling to ethane or ethylene is an appealing, direct route to utilization of otherwise low value natural gas located in remote sites. Researchers have focused on oxidative coupling of methane for about 15 years, using metal oxide catalysts to facilitate the reaction (*1-6*). Despite intensive efforts, the best yields to C2 hydrocarbons have been in the 20 to 30 % range, generally accomplished with catalysts which include an alkali metal on an alkali earth oxide, e.g., Li/MgO (*6b*).

In an attempt to understand and overcome the source of this limitation, more fundamental catalyst studies and modeling have been undertaken. Labinger and Ott (*7*) measured kinetic rate constants and modeled the catalytic process for ARCO's oxidative coupling catalyst, achieving good agreement with reactor data. Labinger in a further analysis (*8*) based on their model found that the C2 yield is limited to 30% by sequential oxidation of ethylene as methane conversion increases. Kimble and Kolts were also able to model the catalytic-homogeneous process for their system (*9*).

The importance of the thermally-induced, homogeneous, gas-phase reactions cannot be neglected in any such model. Much of the recent work in oxidative coupling has explicitly recognized the fact that under most conditions, thermally-induced reactions account for a large fraction of products (*10-14*). In previous work (*15-16*), we employed a chemical kinetic model (HCT), developed at this Laboratory, to describe the overall homogeneous gas phase reactions of methane and oxygen. The HCT model can be used to describe reaction pathways and determine products for a wide variety of reactor types and conditions. Its application successfully predicted methane conversions and product distributions found experimentally for a reactor containing no catalyst. In this work, we expand the HCT model to include proposed catalytic reaction schemes. Our purpose is to predict limits in C2 yield, describe product trends as a function of generalized catalyst behavior and use these results as a guide to catalyst design.

Gas-Phase Model

The gas-phase chemical kinetic model used in the present study is the HCT (Hydrodynamics, Chemical kinetics and Transport) model (*17*). This model solves the coupled equations of conservation of mass, momentum and energy in finite difference form, and determines each chemical species concentration. For this study, the reactor is assumed to be essentially a plug flow system where spatial variations in velocity, temperature and species concentrations in the radial direction and diffusion of energy and species in the axial direction are assumed to be negligible. Spatial changes in species concentration and temperature can therefore be replaced by time variations. Thus only the energy equation and the species conservation equations must be solved. Surface reactions at the reactor wall were not considered. In the numerical model, coupling between the different chemical species takes place through the chemical kinetic terms, and these terms are introduced into the model through a detailed reaction mechanism.

The chemical reaction mechanism used here has developed from a number of studies of methane

and natural gas combustion. This mechanism has been extensively validated in a series of studies where numerical results were compared to experimental results from static reactors, stirred reactors, shock tubes, flames and flow reactors (18-22).

Inclusion of Catalytic Methane Activation

A schematic of the mechanistic pathways leading to the gas-phase oxidation of methane by oxygen is shown in Fig. 1. We have added reactions to the chemical kinetic mechanism to treat the effect of introducing a catalyst. It is generally assumed that the effectiveness of oxidative coupling catalysts stems from their ability to activate methane. Thus, the first step was to determine the effect of methane activation alone. Considerable experimental evidence suggests that the catalyst activates methane by abstracting a hydrogen (2,4,6a,i,7,9,11,23,24). We have modeled this process as the global step,

$$CH_4 + 1/4\ O_2 \rightarrow CH_3 + 1/2\ H_2O \qquad (1).$$
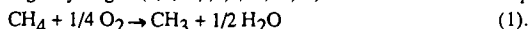
We assumed the reaction rate is given by the expression,

$$R_1 = k_1\ [CH_4][O_2]^a \qquad (2).$$

The dependence of the rate on $[O_2]^a$ serves to turn off the catalytic reaction when the gas phase oxygen is depleted. An exponent "a" of 1.0 serves this purpose satisfactorily, since we do not know the series of elementary reactions. Computationally, it appears that the overall reaction is not critically dependent on the value of the "a" exponent.

. A series of calculations were performed with the above "catalytic" reaction added to the gas-phase chemical kinetic mechanism in order to explore the effect of catalyst activity (k_1) on predicted C_2 yield. The conditions considered were a 2:1 molar ratio of CH_4:O_2 in a 75% Ar mixture. The reactor temperature and pressure were maintained at a constant 750 C and 1 atm, resp. The curve in Fig. 2 shows the results of these calculations, where the residence time for the upper curve was optimized for maximum yield and the residence time for the lower curve was 10 s. The methane conversion and product distributions are shown in Table 1. It is predicted that for k_1 equal to 10^7 $M^{-1}s^{-1}$, the maximum C_2 yield is 84%. When no catalyst is present, the gas-phase reactions result in a C_2 yield of about 0.4% under these conditions of high dilution. The calculations indicate that the catalyst does not substantially affect the yield until the catalytic methane activation rate constant reaches about 10^1. The C_2 yield reaches about 70% for a methane activation rate constant of 10^7. This yield would certainly be adequate to justify production; obviously, either catalysts do not achieve such a high rate constant or they perform another function, such as oxidation.

Although the gas-phase reactions in the absence of catalyst yield only 0.4% C_2's, once the catalyst has generated the methyl radical, it is available for any further reactions. At a sufficiently high level of catalyst activity, the high concentration of methyl radicals will drive the coupling reaction in preference to oxidation steps. Then at short residence times, the catalytic methane activation and gas-phase coupling steps will be sufficient to predict products. Thus it is of interest to know the relative contribution of gas-phase vs catalytic reactions to the overall conversion of methane. To determine these relative contributions, we integrated over time the rates of methane conversion due to the catalyst and to gas-phase reactions for values of k_1 of 10^3, 10^4 and 10^5. These results are shown in Fig. 3. As expected, the catalyst contributes virtually all of the methane conversion at early times until a sufficient radical pool is established for gas-phase reactions. A steady state conversion is reached by about 7 s, 0.3 s and 0.06 s for k_1 of 10^3, 10^4 and 10^5, resp. At steady state, 20%, 50% and 70% of the methane is converted due to catalytic action for values of k_1 equal to 10^3, 10^4 and 10^5, resp. The

catalyst dominates methane conversion for values of the methane activation rate constant greater than 10^4.

Now we investigate the effect of moving away from our optimized residence time. The methane conversion and product distributions corresponding to the predicted maximum C_2 yields for values of k_1 of 10^2 to 10^5 are shown in Table 1. The methane conversion increases from 23.3 to 53.7%, while the selectivity to C_2's increases from 44.5 to 67.1%. The major increase in C_2's is due to an increase in ethane from 18.7 to 41.6%. The residence times which result in maximum C_2 yields decrease from 3.4 to 0.03 s as k_1 increases from 10^2 to 10^5. Since the gas-phase coupling reaction to form ethane is rapid relative to dehydrogenation to ethylene, at shorter residence times, one would expect a higher ethane/ethylene split. The calculated methane conversion and product distributions at 10s residence time, displayed in Table 2, show that this is indeed true. At longer residence times, the C_2 yield decreases slowly, the methane conversion increases, and the C_2 selectivity decreases along with selectivity to ethane. Regardless of residence time, carbon monoxide accounts for the majority of COX products.

Comparison of Model Predictions with Experimental Data

Values of k_1 and the corresponding C_2 yield for catalysts known to be effective in oxidative coupling of methane (6b-h) and run under similar conditions to those run for the model are also shown in Fig. 2. In calculating k_1 from literature data, it was assumed that the rate of methyl radical production was equal to the rate of methane conversion and was, therefore, determined from the experimental methane feed rate and the final methane conversion. The rate constant k_1 was then found by dividing that rate by the methane and oxygen concentrations in the feed at reaction temperature. As shown in Fig. 2, the fit of model predictions to rate constants calculated from experimental results is quite good. The values of k_1 that we determined range from 10^2 to 10^5, corresponding to measured C_2 yields of 3-20%, while the model predicts C_2 yields increasing from 8-35%. The methane activation rate constants for these coupling catalysts are too low to achieve the high C2 yields possible from our model calculations. Even the more active catalysts do not give C2 yields of 35%, as the model predicts. In fact, for methane activation rate constants of 10^3 and greater, the experimental C2 yield is fairly flat as a function of catalyst activity. Table 3 shows a selection of data for coupling catalysts (6b-d). The fit of the model to C_2 yield, methane conversion and selectivity to C_2's is quite reasonable, matching best at model residence times slightly greater than those optimized for C_2 yield. In a few cases, the predicted ethane/ethylene split is very close to literature values, and fairly good for the others.

The model does not predict carbon dioxide as the only oxidation product, as is seen in the data. It seems likely that the carbon dioxide is produced directly by a catalytic route, bypassing the gas-phase reactions that would lead from ethylene to carbon monoxide. Such a catalytic process could also explain the cap on C_2 yield observed for the coupling catalysts.

Summary

Overall, this simple modification of the gas-phase kinetic model to include a global catalytic step that only produces methyl radicals agrees reasonably well with experimental data. The model predicts that a methane activation catalyst with a sufficiently high rate constant, which performed no other function, could result in a C_2 yield of at least 70%. The high methane activation rate constant is needed

to overcome gas-phase oxidation reactions. The highest methane activation rate constant determined from experimental data was on the order of 10^5 M^{-1}s^{-1}, corresponding to a predicted C_2 yield of 35%, but actually yielding only about 20%. A catalytic reaction leading from ethylene to carbon dioxide could account both for the lowered yield and for the absence of carbon monoxide in experimental work.

References

1. Pitchai, R.; Klier, K. Catal.Rev.Sci.Eng. 1986, 28, 13.
2. Lee, J.S.; Oyama, S.T. Catal.Rev.Sci.Eng. 1988, 30, 249.
3. Hutchings, G.J.; Scurrell, M.S.; Woodhouse, J.R. Chem.Soc.Rev. 1989, 18, 251.
4. Lunsford, J.H. Catal.Today 1990, 6(3), 235.
5. Garibyan, T.A.; Margolis, L.Y. Catal.Rev.Sci.Eng. 1989-1990, 31, 355.
6. a). Keller, G.E.; Bhasin, M.M. J.Catal. 1982, 73, 9.
   b). Ito, T.; Lunsford, J.H. Nature 1985, 314, 721.
   c). Otsuka, K.; Liu, Q.; Morikawa, A.; Inorg.Chim.Acta 1986, 118, L23.
   d). Machida, K.l.; Enyo, M. J.Chem.Soc., Chem.Commun. 1987, 1639.
   e). France, J.E.; Shamsi, A.; Ahsan, M.Q. Energy & Fuels 1988, 2, 235.
   f). Matsuura, l.; Utsumi, Y.; Nakai, M. Doi, T. Chem.Lett. 1986, 1981.
   g). Otsuka, K.; Komatsu, T. J.Chem.Soc.,Chem.Commun. 1987, 388..
   h). Aika, K.; Moriyama, T.; Takasaki, N. Iwamatsu, E. J.Chem.Soc., Chem.Commun. 1986, 1210.
   i). Sofranko, J.A.; Leonard, J.J.; Jones, C.A. J.Catal. 1987, 103, 302.
   j). Thomas, J.M.; Kuan, X.; Stachurski, J. J.Chem.Soc., Chem.Commun. 1988, 162.
   k). Korf, S.J.; Roos, J.A.; Derksen, J.W.H.C.; Vreeman, J.A.; Van Ommen, J.G.; Ross, J.R.H. Appl.Catal. 1990, 59, 291.
   l). Ahmed, S.; Moffat, J.B. J.Catal. 1990, 125, 54.
   m). Agarwal, S.K.; Migone, R.A.; Marcelin, G. J.Catal. 1990, 121, 110.
   n). Choudhary, V.R.; Chaudhari, S.T.; Rajput, A.M.; Rane, V.H. J.Chem.Soc.,Chem.Commun. 1989, 1526.
7. Labinger, J.A.; Ott, K.C. J.Phys.Chem. 1987, 91, 2682.
8. Labinger, J.A., Cat.Lett. 1988 1, 371.
9. Kimble, J.B.; Kolts, J.H. Energy Prog. 1986, 6 (4), 226.
10. Lane, G.S.; Wolf, E.E. J.Catal. 1988, 113, 144.
11. Zanthoff,H.; Baerns, M. Ind.Eng.Chem.Res. 1990, 29, 2.
12. Yates, D.J.C.; Zlotin, N.E. J.Catal. 1988, 111, 317.
13. Nelson, P.F.; Cant, N.W. J.Phys.Chem. 1990, 94, 3756.
14. Ekstrom, A.; Lapszewicz, J.A.; Campbell, I. Appl.Catal. 1989, 56, L29.
15. Droege, M.W.; Hair, L.M.; Pitz, W.J.; Westbrook, C.K. Lawrence Llvermore National Laboratory Report UCRL-100568 1989.
16. Droege, M.W.; Hair, L.M.; Pitz, W.J.; Westbrook, C.K. in Proc. 1989 SPE Gas Tech. Symp. 1989, Dallas, TX., p. 247.
17. Lund, C.M. University of California Lawrence Livermore National Laboratory Report UCRL-52504. 1978 Revised by Lila Chase, 1989.

18. Westbrook, C.K.; Pitz, W.J. **Combust.Sci.Technol. 1984,** 37, 117.

19. Westbrook, C.K.; Creighton, J.; Lund, C.; Dryer, F. **J.Phys.Chem. 1977,** 81, 2542.

20. Westbrook, C.K. **Combust.Sci.Technol. 1979,** 20, 5.

21. Wilk, R.D.; Cernansky, N.P.; Pitz, W.J.; Westbrook, C.K. **Combustion Flame 1989,** 77, 145

22. Pitz, W.J.; Westbrook, C.K.; Proscia, W.M.; Dryer, F.L. **Twentieth Symposium (International) on Combustion,** The Combustion Institute: Pittsburgh, 1985, p.831.

23. Driscoll, D.J.; Martin, W.; Wang, J.-X.; Lunsford, J.H. **J.Am.Chem.Soc. 1985,** 107, 58.

24. Mims, C.A.; Hall, R.B.; Rose, K.D.; Myers, G.R. **Catal.Lett. 1989,** 2, 361.

Table 1
Predictions of Model at Maximum C2 Yield

$k1$ $(M^{-1}s^{-1})$	Max %C2 Yld	%CH4 Conv	%C2	%C2H4	%C2H6	%CO	%CO2
10^2	10.4	23.3	44.5	25.8	18.7	51.5	3.1
10^3	15.8	25.0	63.2	32.2	31.0	34.8	0.9
10^4	24.7	35.1	70.2	33.4	36.8	28.2	0.5
10^5	35.1	52.3	67.1	25.5	41.6	14.6	0.1

Table 2
Predictions of Model at 10s Residence Time

$k1$ $(M^{-1}s^{-1})$	%C2 Yld	%CH4 Conv	%C2	%C2H4	%C2H6	%CO	%CO2
10^2	7.5	46.4	16.1	13.2	2.9	71.9	11.6
10^3	11.0	51.3	21.5	19.0	2.5	71.0	6.9
10^4	17.9	57.3	31.3	27.5	3.8	64.6	3.1
10^5	30.6	67.5	45.5	39.4	6.1	52.1	1.1

Table 3
Experimental Results from Literature

Ref	%C2 Yield	%CH4 Conv	%C2	%C2H4	%C2H6	%CO	%CO2
6b	19.0	37.8	50.5	31.0	19.5	0.0	49.6
	19.4	42.8	45.5	29.0	16.5	0.8	53.7
6c[i]	18.6	25.9	71.8	56.2	15.6	-.-	-.-
6c[ii]	13.2	25.8	51.3	23.4	27.9	-.-	-.-
6d	31.8	45.1	60.1	36.1	24.0	0.0	39.9

6b. 7%Li/MgO, 4g: 720 C, 2:1 $CH_4:O_2$, 89% He Diln.

6c. (i) 20 mol% LiCl/NiO (ii) 20 mol%LiOH/NiO: 750 C, $CH_4:O_2$ 2:1, 94% He diln., 1 g cat.

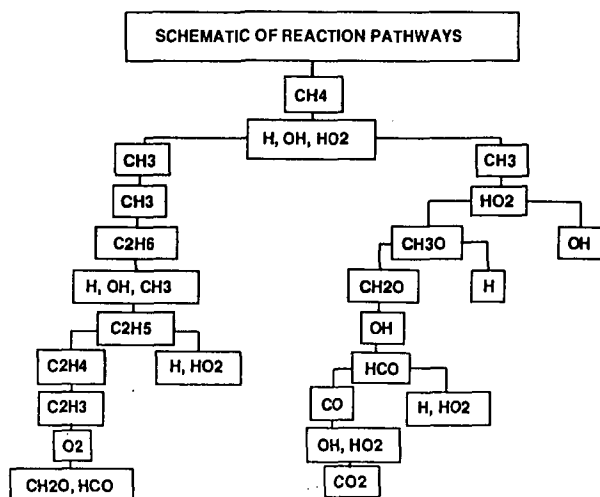6d. SrCeYbO, 0.6 g: 750 C, $CH_4:O_2$ 2:1, 80% diln with He.

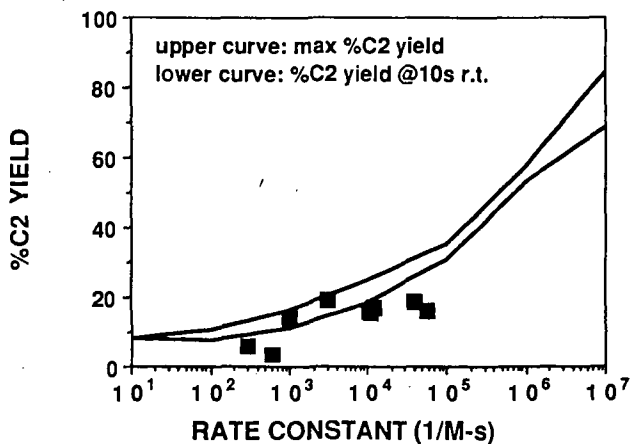Figure 1. Schematic of gas-phase mechanism for methane oxidation.

Figure 2. Predicted and experimental C_2 yields as a function of catalytic methane activation rate constant, k_1. Conditions: 750 C, 2:1 $CH_4:O_2$, 75% Ar dilution.
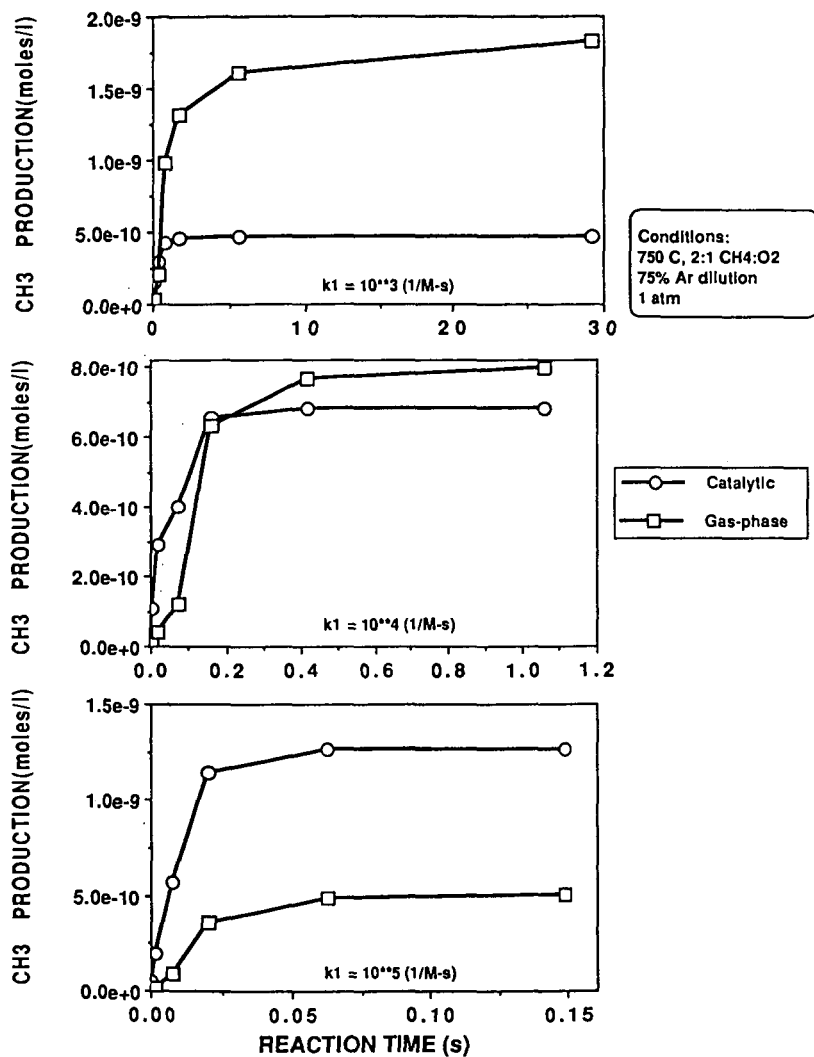
Figure 3. Comparison of methyl production due to catalytic and gas-phase reactions. a) $k_1=10^3$. b) $k_1=10^4$. c) $k_1=10^5$. Units=$M^{-1}s^{-1}$.